P Determination in Fertilizers by AAS

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Direct Determination of Phosphorus in Fertilizers by Atomic Absorption Spectroscopy

Daniel Hoft, Joe Oxman, and Rogers C. Gurira*

Phosphorus (expressed as P_2O_5) content in commercial fertilizers has been determined by the method of atomic absorption spectroscopy (AAS). The application of the technique takes advantage of the low background absorption by the premixed nitrous oxide–acetylene flame and the phosphorus nonresonance line at 213.6 nm. Phosphorus in eight commercial fertilizers, with reported percentages ranging from 10 to 46 and two National Bureau of Standards phosphorus standards, was determined with excellent precision and accuracy. No significant spectral, matrix, or chemical interferences were observed. The AAS method of determining phosphorus in fertilizer has the advantage of speed, specificity, and freedom from interferences.

Currently, phosphorus in fertilizers is routinely determined either by the gravimetric quinolinium molybdophosphate or the molybdovanadophosphate spectrophotometric methods (AOAC, 1975). Both of these methods share certain drawbacks. The spectrophotometric method is not applicable to fertilizers that are either colored or that yield colored solutions or contain ions other than orthophosphate which form colored complexes with molybdovanadate reagent. This is a major limitation since a substantial number of fertilizers are colored. The gravimetric method, in spite of its accuracy and precision, is inherently slow; it involves several steps and also requires several reagent solutions. Furthermore, both methods require that phosphorus be in the form of orthophosphate. This requirement calls for elaborate digestion steps except for the determination of water-soluble phosphates. In view of the limitations inherent in the techniques currently available for phosphorus determination in fertilizer, we have investigated and established the use of an atomic absorption method. The method is rapid (requiring minimal chemical manipulation and no separation), specific for phosphorus, and free from interferences.

The determination of phosphorus by atomic absorption spectroscopy (AAS) has been difficult to achieve in the past because the ground-state lines of phosphorus lie at wavelengths less than 200 nm, the region where flames and atmospheric gases such as oxygen absorb light very strongly. Therefore, in order to measure phosphorus directly at its ground-state lines, the flame employed must not only be hot enough to atomize the phosphorus efficiently, but must also be transparent to the primary source at these wavelengths. Nitrogen purging of the optical path is also necessary to remove oxygen. In practice this is difficult to accomplish.

These problems prompted Manning and Slavin (1969) to investigate the use of the premixed nitrous oxide–acetylene flame in the determination of phosphorus at its nonresonance line of 213.6 nm. The flame showed marked reduction in noise and background absorption. In addition, the need for nitrogen purging of the optical path was eliminated by performing measurements at this wavelength. The major disadvantage in using this line was due to poor sensitivity (290 $\mu g/mL$). In spite of this limitation, however, the method was highly reproducible for the direct determination of phosphorus in high concentrations. Furthermore, Kerber et al. (1970) established that AAS determination of phosphorus was practically free from chemical interferences. On the basis of all this information we decided to explore the potential applicability of this technique to analytical determination of samples containing large amounts of phosphorus, such as fertilizers. Our findings are the subject of this report.

EXPERIMENTAL SECTION

Apparatus. A Perkin-Elmer Model 103 atomic absorption spectrometer was used in conjunction with a phosphorus hollow cathode lamp and a nitrous oxide burner head (Perkin-Elmer No. 303-0419). The fuel and the oxidant flow rates were set respectively at 9 and 16 L/min. Once the flame was ignited, the fuel flow was adjusted until the rose-red inner cone was about 2 cm high. Expansion was kept at zero for all the determinations to limit noise from the detector. It was found necessary to clean the burner from time to time in order to remove solids that accumulate on it due to large amounts of dissolved solids.

Reagents. All chemicals used for preparing standard solutions and for the interference studies were of reagent

Department of Chemistry, Grinnell College, Grinnell, Iowa 50112.

grade and were used without further purification. Stock solutions containing 50 000 µg/mL of phosphorus were prepared by dissolving 107.7 g of 99% pure diammonium hydrogen orthophosphate in about 400 mL of deionized water, in a 500-mL volumetric flask, followed by adding enough water to bring the volume to the mark. These stock solutions were then diluted as required to prepare the standard phosphorus solutions for the calibration curves.

Preparation of Fertilizer Samples. Four to six samples of each fertilizer (containing enough phosphorus to fall within the calibration range of 5000 to 10 000 µg/mL) were obtained, dried, and then carefully weighed out. Each sample was dissolved in about 30 mL of deionized water and heated with occasional stirring for about 5 min (to insure total liberation of phosphorus). The undissolved material was filtered off and the clear solution was then transferred into a 100-mL volumetric flask and made up to 100 mL with deionized water. Alternately the samples were heated (digested) in acid solution and then subsequently treated as described above. This treatment yielded the same results as the nonacid method.

Procedure. First, in order to use the atomic absorption method, a study of the range of linearity was conducted. This was accomplished by preparing solutions containing known amounts of phosphorus ranging between 5000 and 50 000 µg/mL of phosphorus. (As will be pointed out in the Discussion section of this report, measurements of concentrations of phosphorus much lower than these are now possible.) The spectrophotometer was set to isolate light at the phosphorus nonresonance line of 213.6 nm. The relative absorbance of each solution was measured and a graph of relative absorbance vs. phosphorus concentration was plotted to determine the concentration range in which linearity would be obtained. The concentration range was found to be between 5000 µg/mL and 30 000 µg/mL of phosphorus. Values above 30 000 µg/mL showed deviations from linearity. Consequently, subsequent measurements were confined to concentration values below 30 000 µg/mL of phosphorus.

This same procedure was used for determining phosphorus in fertilizer samples. The measurements were made at the 213.6 nm phosphorus nonresonance line. First a linear calibration curve was plotted from relative absorbance values of eight standard phosphorus solutions (ranging from 5000 to 10 000 µg/mL). Similarly, absorbance values for the fertilizer samples were measured and the corresponding concentrations of phosphorus were obtained by extrapolation from the calibration curve. From the experimentally determined phosphorus concentration, the percent P_2O_5 in the fertilizer was calculated from:

$$\% \; P_2O_5 = \text{concn of P } (\mu g/mL) \times \frac{100 \text{ mL}}{\text{g of fert.}} \times$$
$$10^{-6} \; (g/\mu g) \times \frac{M_r \text{ of } P_2O_5}{2 \text{ g at. wt of P}} \times 100 \quad (1)$$

where g of fert. is the weight of fertilizer, M_r of P_2O_5 is the molecular weight of phosphorus pentoxide and g at. wt of P is the gram atomic weight of phosphorus. Four to six replicate determinations were obtained for each different fertilizer. The values for the percent P_2O_5 were then compared to the commercially reported ones. In all, eight different fertilizers, with P_2O_5 percentages ranging between 10 to 46%, and two National Bureau of Standards (NBS) primary samples (KH_2PO_4, 186-1-6 and Na_2HPO_4, 186-11-6) were used in this study. The results are summarized in Table I.

Table I. Precision and Accuracy

sample	% P_2O_5 reported	% P_2O_5 found	precision,[a] %
20-10-5	10	10.1 ± 0.1	1.0
5-15-5[b]	15	16.0 ± 0.3	1.5
20-20-20	20	20.1 ± 0.4	2.1
15-30-15	30	28.9 ± 0.4	1.1
12-31-14	31	31.1 ± 0.4	3.8
8-32-16	32	32.0 ± 0.4	1.1
0-44-0	44	44.2 ± 0.6	1.4
18-46-0	46	45.9 ± 0.4	0.9

NBS sample	% P	% P found	accuracy, %
KH_2PO_4	22.8	22.8	0.000
Na_2HPO_4	21.8	21.9	0.0005

[a] Expressed as % relative deviation. [b] Liquid form.

Table II. Interference Studies: Percent Recovery of Phosphorus in Fertilizer Samples When Al, Ca, Cu, and Fe Were Added to the Samples

interfering element	20-10-5	20-20-20	8-32-16	0-44-0	18-46-0
Al	100	89[a]	100	100	100
Ca	100	100	100	95	92
Cu	95	100	100	100	100
Fe	95	100	90	100	100

[a] A precipitate formed in this solution and may have been the reason for the low percent recovery.

Interference Studies. An interference study was conducted using Al, Ca, Cu, and Fe metal ions, which are common trace elements found in commercial fertilizers. This study was done at low levels of these elements in order to create a realistic excess amount of phosphorus. Solutions, consisting of concentration ratios of 1:4 for the interfering element to phosphorus respectively, were prepared. Their relative absorbances were measured and compared with those of the solution containing the same amount of fertilizer but with no interfering element present. These results are summarized in Table II.

RESULTS AND DISCUSSION

The precision values for all fertilizers, expressed as percent relative deviation, fell in the range between 0 and 4. The values also compared favorably with those reported by the manufacturers as shown in Table I. The reliability and accuracy of the AAS method for measuring phosphorus was further demonstrated by determining the phosphorus content in two primary samples obtained from the National Bureau of Standards. Two replicates were performed for each of these and the results obtained were quite precise and accurate as shown at the bottom of Table I.

This study indicates that the direct determination of phosphorus by AAS at the 213.6 nm nonresonance line is readily applicable to the routine analysis of fertilizers. The high temperature of the nitrous oxide–acetylene flame considerably enhances the sensitivity of the atomic absorption detection of phosphorus by limiting chemical and physical interferences, as well as background absorption from the flame. The attractive features of this technique lie in its specificity, simplicity, and rapidity. For water-soluble phosphates, this method eliminates the need for acid hydrolysis or digestion processes. On the other hand, water-insoluble phosphates can be subjected to the standard acid hydrolysis procedure, followed by the treatment outlined in this publication. The interference study shows the technique to be free from chemical in-

terferences. The accuracy and precision of the AAS technique make it very attractive for measuring high concentrations of phosphorus, such as those existing in fertilizers. Because of these advantages, it is conceivable that this method may someday be used on a routine basis for these determinations.

Furthermore, since our studies were conducted, two ways of improving both sensitivity and detection limits for phosphorus determination have been demonstrated. Barnett et al. (1976) have shown that the detection limit can be improved respectively 2.8- and 5-fold by the use of electrodeless discharge lamps (EDL) with either flame AA or nonflame graphite furnace technique. In addition, Ediger (1976) has demonstrated that sensitivity and detection limits can be further improved substantially by the use of a combination of EDL with graphite furnace and the addition of 1% lanthanium as nitrate. Using this combination and the Perkin-Elmer Model 603 atomic absorption spectrophotometer, Ediger obtained sensitivity and detection limit values of 7500 pg and 10 ng (0.1 μg/mL), respectively. Therefore the use of either of these methods for phosphorus determinations would substantially reduce the sample sizes and the concentrations of samples used in general. The application of these techniques to fertilizer analysis should make AA even more advantageous to use than the existing methods.

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Production of Magnesium Phosphate from Apatite and Carnallite. 1. Chemistry and Mineralogy

Ithamar Pelly* and Petahia Bar-On

Magnesium phosphate was produced from Oron phosphate and carnallite. Chemical and mineralogical aspects were studied as a function of reaction temperatures, F/P ratios, Mg/Ca ratios, reaction times, and grinding the phosphate. Although two reaction mechanisms are suggested in the literature, it appears that no clear-cut conclusion can be reached and that neither explains all the observed facts. The most likely mechanism seems to be one in which the first step is the formation of chlorapatite and MgF_2. The chlorapatite reacts to give magnesium phosphate which reacts with MgF_2 to form wagnerite. Magnesium phosphate and wagnerite are in equilibrium; the higher the temperature, the higher is the magnesium phosphate yield in the product.

Most of the phosphate fertilizers are manufactured from phosphate rocks. In phosphate sedimentary rocks the major mineral is usually francolite (fluorcarbonate-apatite). Its composition varies but can be summarized as $(Ca, Na, Mg)_{10}(PO_4)_{6-x}(CO_3)_xF_y(F, OH)_2$, where y is the range of $0.33x-0.5x$.

The mole ratio F/P in Israeli phosphates is about 0.41 and is higher than in fluorapatite (0.33). It is suggested (Ando and Matsuno, 1966; Smith and Lehr, 1966) that in such cases some of the phosphate ions are replaced by Co_3F^{3-} ions.

Apatites containing fluorides are only slightly soluble in water and in organic acids so that the phosphate is not readily available to plants. In the fertilizer industry the apatite is destroyed (there are several methods) to create more soluble compounds. For comparison purposes the availability to plants is measured by the solubility in citric acid or in ammonium citrate.

Magnesium phosphate (MP), $Mg_3(PO_4)_2$ (which is soluble in citric acid), is produced in Japan by reacting the phosphate with olivine or serpentine at 1400 °C. MP can also be produced in a reaction between apatite and magnesium chloride brine (Lavie, 1961).

Baniel et al. (1965) suggested the use of carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, for this reaction. $MgCl_2 \cdot 6H_2O$ cannot be used because on drying it reacts with its own water to form MgO (periclase) which does not react with apatite. Carnallite is more stable on drying (at about 180 °C). The reaction between carnallite and apatite is carried out at 600 °C. The product is washed with water and up to 80% of the potassium can be recovered, thus the reaction can be carried out at almost no loss of potash yield.

Only a few studies (Ando and Hoego, 1972; Stavski, 1970) have been done to investigate the mechanism and mineralogical changes involved in the reaction. The main phosphate minerals formed are wagnerite (W) (Mg_2PO_4F) and magnesium phosphate (MP). Stavski (1970) studied the influence of the amounts of Ca, Mg, and F and the temperature, but he used mixtures of $Ca_3(PO_4)_2$ and CaF_2 instead of apatite so the results may not hold for the apatite case. He found that chlorapatite, $Ca_{10}(PO_4)_6Cl_2$, and Ca_2PO_4Cl, calcium chlorwagnerite, can also be formed. Ando and Hoego (1972) did a semiquantitative analysis (using X-ray diffractograms) of products of reactions at several temperatures. They found that chlorapatite was a major reaction product (together with MP and W) and suggested the following mechanism:

$$Ca_5(PO_4)_3F + 5MgCl_2 \rightarrow$$
$$Mg_3(PO_4)_2 + Mg_2PO_4F + 5CaCl_2 \quad (1)$$
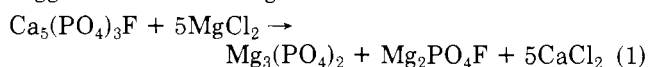
Department of Geology and Mineralogy, Ben Gurion University of the Negev, Beer Sheva, Israel.